ABSTRACT

Alkylation of Aromatics is of immense importance to the petrochemical industry. The importance is well defined in the case of production of ethylbenzene, cumene and cymenes because of their varied uses. Alkylation processes were traditionally conducted over Friedel-Crafts catalysts. Presently, these are being replaced by acidic molecular sieves having high thermal stabilities, shape selective properties, regenerability, non-corrosive and eco-friendly nature. These industrial processes use mainly alkenes as the alkylating agents. However, alkenes have the disadvantages of transportation, handling and are unavailable in abundance compared to the alcohols. The use of different alcohols as alkylating agents also proved to enhance the catalyst stability. The present work is, therefore, focused on the alkylation reactions of benzene and toluene with lower alcohols over large pore molecular sieves. To enhance the yields of the commercially important main alkylation products, further transalkylation of the disubstituted by-products is essential. Hence, in the cumene process diisopropyl benzene isomers obtained as main by-products were further transalkylated with benzene to increase the cumene yields.

All the atmospheric runs were conducted in a glass reactor and the high pressure studies were conducted in SS pressure reactor set-up. Analysis of the reaction products was done using a Gas Chromatograph Unit with FID and TCD.

Zeolite Hbeta with its asymmetric channel structure was found to be selective to cumene in the isopropylation of benzene with isopropyl alcohol. Hence, the effect of various process parameters on the yield and selectivity of cumene and the reaction kinetics were investigated in detail over this zeolite. The same catalyst loaded with platinum (0.005%) was also investigated in the transalkylation of diisopropyl benzene isomers obtained from cumene column bottom fraction of a commercial plant.

Recently, the alumino-phosphate class of molecular sieves have been found to be active in many classical reactions and hence the acidic, silicon substituted alumino phosphates were also studied in these alkylation reactions. The results show that higher silicon substituted alumino phosphate molecular sieves are active and cumene selective in the benzene isopropylation reaction as well as in the transalkylation of diisopropyl benzene to cumene.

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Kinetic modeling led to homogeneous model over Hbeta and L-H-H-W surface reaction models over SAPO-5 as best for interpreting the mechanism of benzene isopropylation reaction. The large pore SAPO-5 has proved to be a promising catalyst in cumene and cymene synthesis reactions. Both Hbeta and SAPO-5 were also found to be potential catalysts in transalkylation of diisopropyl benzene with benzene.

Another large pore zeolite HM with high Si/Al (44.9) ratio was also studied and found to be stable and cymene selective in toluene isopropylation with isopropyl alcohol. When the aromatic was taken in excess, pseudo-first order rates with respect to the limiting reactant, i.e., alcohol, were found to fit the experimental data well for these reactions.

The kinetics of ethylation of benzene was studied over AlCl₃ impregnated 13X zeolite in an integral pressure reactor. In this case too, L-H-H-W surface reaction model was found to interpret the kinetics reasonably well.

The non-linear estimation of kinetic parameters was done by using Marquadt's routine, minimizing the error function defined by the sum of the squares of the difference between the experimental and predicted conversions. The apparent activation energies and pre-exponential factors for all these reactions were evaluated using the Arrhenius equation.

Key words: alkylation, transalkylation, benzene, toluene, cumene, cymene, ethylbenzene, diisopropyl benzene, ethyl alcohol, isopropyl alcohol, molecular sieves, 13X zeolite, beta, SAPO-5, mordenite, synthesis, characterization, kinetics, kinetic model, surface reaction, catalyst deactivation

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